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- (71) Applicant (for all designated States except US): ALCOA OF AUSTRALIA LIMITED [AU/AU]; Cnr Davy and Murrumbidgee Streets, Booragoon, W.A. 6154 (AU).
- (74) Agent: WRAY & ASSOCIATES; 239 Adelaide Terrace, Perth, W.A. 6000 (AU).
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(54) Title: AGGLOMERATION OF ALUMINA AND BINDER THEREFOR

(57) Abstract: A method for the agglomeration of alumina particles, the method comprising the steps of: adding a quantity of pseudo-boehmite to the alumina particles; and spray drying the mixture so formed to produce agglomerated granules.

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**"Agglomeration Of Alumina And Binder Therefor"****Field of the Invention**

The present invention relates to a method for the agglomeration of particles of alumina, or particles containing a substantial portion of alumina, and a binder for  
5 use in such.

**Background Art**

In the Bayer process for the extraction of alumina from alumina containing ores, precipitated alumina tri-hydrate is filtered, dried and calcined. This yields high purity alumina with a narrow range of particle sizes. However, a by-product of the  
10 calcination process is extremely fine particles of alumina, with an average size of less than 30  $\mu\text{m}$ . This by-product is caught in the gas cleaning devices, including multi-cyclones, electrostatic precipitators and/or bag-houses, attached to the calcination device. Such particles are commonly known as ESP dust. In addition to being difficult to handle, ESP dust is difficult to reintroduce into the process  
15 stream, not being readily redigested in the highly caustic solution of the digestion phase.

Accordingly, it is desirable to be able to agglomerate small particles of alumina, such as ESP dust, to form coarser particles. Ideally, these coarser particles are of a size range suitable for use in aluminium smelting.

20 In the ceramics industry, particles are agglomerated by spray drying using organic polymers as binders. However, the agglomerates formed by these methods are typically weakly bonded and they are readily degraded when handled or transported.

In Australian Patent 664328, there is provided a method for agglomerating  
25 alumina particles with a binder comprising a polymer form of a hydroxy salt of aluminium. In a variant of the invention, activated alumina is used to reduce the quantities of the binding agent required. The activated alumina is believed to

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enhance binding by forming a film of pseudo boehmite that adheres to the particles of unactivated alumina powder. However, it is clearly stated that the activated alumina cannot be used alone to achieve beneficial agglomeration of the alumina particles.

- 5 However the cost of the binding agent, and that associated with the production of activated alumina, have prevented the widespread application of this method. It is one object of the present invention to provide a method for the agglomeration of particles of alumina, or particles comprising alumina, where the quantity of binder required is substantially reduced, and the need for activated alumina eliminated.
- 10 The preceding discussion of the background to the invention is intended to facilitate an understanding of the present invention. However, it should be appreciated that the discussion is not an acknowledgement or admission that any of the material referred to was part of the common general knowledge in Australia as at the priority date of the application.
- 15 Throughout the specification, unless the context requires otherwise, the word "alumina" will be understood to encompass fully dehydrated alumina, fully hydrated alumina, partially hydrated alumina or a mixture of these forms.

Throughout the specification, unless the context requires otherwise, the term "alumina particles" will be understood to include particles of an alumina containing

20 material where the alumina content of said particles is at least about 30% by weight  $\text{Al}_2\text{O}_3$ .

Further, throughout the specification, unless the context requires otherwise, the word "comprise" or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not

25 the exclusion of any other integer or group of integers.

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**Disclosure of the invention**

In accordance with the present invention, there is provided a method for the agglomeration of alumina particles, the method comprising the steps of:

adding a quantity of pseudo-boehmite to the alumina particles; and

5        spray drying the mixture so formed to produce agglomerated granules.

Preferably, the pseudo-boehmite is added as an aqueous suspension.

Preferably, the aqueous suspension of pseudo-boehmite is formed at a temperature between about 15 and 100°C. Preferably still, the aqueous suspension of pseudo-boehmite is formed at a temperature above about 80°C. In  
10        a highly preferred form of the invention, the aqueous suspension of pseudo-boehmite is formed at a temperature above about 85°C.

Preferably, a quantity of acid is added to the aqueous suspension of pseudo-boehmite such that the pH of such is between about 2 and 6. Advantageously, a quantity of acid is added to the aqueous suspension of pseudo-boehmite such  
15        that the pH of such is approximately 3. Preferably, the acid is monoprotic. In a highly preferred form of the invention, the acid is acetic acid.

Preferably, before the step of adding a quantity of pseudo-boehmite to the alumina particles, the present invention comprises the step of grinding the alumina particles to a  $D_{50}$  of less than 12  $\mu\text{m}$ . Preferably, the alumina particles  
20        are ground to a  $D_{50}$  of less than about 9  $\mu\text{m}$ . In a highly preferred form of the invention, the alumina particles are ground to a  $D_{50}$  of about 5  $\mu\text{m}$ .

In one form of the invention, a quantity of water is added to the alumina particles to form a slurry, the slurry then being subjected to grinding.

In an alternate form of the invention, the alumina particles are subjected to dry  
25        grinding before a quantity of water is added to form a slurry. Where the alumina particles are subjected to dry grinding before a quantity of water is added to form

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a slurry, the quantity of water may be provided by way of the aqueous suspension of pseudo-boehmite.

Preferably, the slurry is of as high a density as possible. Preferably still the slurry comprises at least 50% solids. Typically, the slurry comprises between about 40  
5 and 60% solids.

The slurry may also contain a viscosity modifier. The viscosity modifier may be one or more of acetic acid, citric acid or a polyacrylate. Preferably, sufficient viscosity modifier is added such that the viscosity of the slurry is less than about 4 cp. In a preferred form of the invention, the viscosity modifier is acetic acid. In a  
10 highly preferred form of the invention, sufficient acetic acid is introduced such that the concentration of the acetic acid in the slurry is between about 0.2 and 1.5% by weight of the alumina particles.

Preferably, before the quantity of pseudo-boehmite is added to the alumina particles, the method comprises the additional steps of:

15 neutralising, dewatering and washing the alumina particles.

In one form of the invention, dewatering is achieved by way of filtration. In an alternate form of the invention, dewatering may be achieved by way of centrifugation. Preferably, carbon dioxide is used to neutralise the alumina particles.

20 The step of neutralising, dewatering and washing the alumina particles may be carried out before or after grinding the alumina particles. Conveniently, the step of neutralising, dewatering and washing the alumina particles is carried out before the step grinding the alumina particles as a smaller filter may be used.

The method of the present invention may comprise the additional step of:

25 heating the agglomerated granules.

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In one form of the invention, the agglomerated particles are dehydroxylated by heating to approximately 300°C. In an alternate form of the invention, the agglomerated granules are calcined above 500°C.

#### **Best Mode(s) for Carrying Out the Invention**

- 5 The method of the present invention will subsequently be described, by way of example only, with reference to one embodiment thereof and several examples.

In the embodiment, a quantity of water is added to particulate alumina to form a slurry of a density between about 40 and 60% solids. A viscosity modifier, in the form of acetic acid is added to the slurry such that the concentration of acetic acid

- 10 In the slurry is between about 0.2 and 1.5% by weight of the alumina particles.

The slurry is then subjected to grinding such that the alumina particles are ground to a  $D_{50}$  of less than 12 $\mu$ m and preferably about 5 $\mu$ m.

A quantity of binding agent in the form of an aqueous suspension of pseudo boehmite is added to the slurry.

- 15 The aqueous suspension of pseudoboehmite is formed at a temperature above about 80°C, and preferably above about 85°C. A quantity of monoprotic acid, preferably acetic acid, is added to the aqueous suspension of pseudo boehmite such that the pH is about 3.0.

- 20 The mixture formed by the addition of the aqueous suspension of pseudo boehmite to the slurry is then spray dried to produce agglomerated granules.

The agglomerated granules may then be heated to in excess of approximately 300°C to effect dehydroxylation of such, or in excess of approximately above 500°C to effect calcination of such.

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The present invention will now be described by way of eleven examples. However, it must be appreciated that the following description of those examples is not to limit the generality of the above description of the invention.

### Examples

#### 5 Example 1

One kilogram of alumina particles with a  $D_{50}$  of 15.3  $\mu\text{m}$  was added to 1200 mL of water to form a slurry. Carbon dioxide gas was bubbled through the slurry until the pH of such was about 6.5. Glacial acetic acid (5g) was added to the slurry, which was then heated to 85°C.

- 10 A quantity of a pseudo-boehmite suspension was added to the slurry. The pseudo-boehmite suspension was prepared by the dispersion of 50 g of a commercial pseudo-boehmite (either Catapal B (supplied by Vista Condea) or HiQ X (supplied by Alcoa World Chemicals)) in 200 g of 85°C water. After the mix returned to 85°C, 5 g of glacial acetic acid was added.
- 15 After mixing for several minutes the slurry to which the pseudo-boehmite suspension was added was then spray dried. Throughout the spray drying the off gas temperature was maintained at 180°C. Portions of the product were calcined at 500°C in a muffle furnace for one hour.

#### Example 2

- 20 One kilogram of alumina particles with a  $D_{50}$  of 15.3  $\mu\text{m}$  was added to 1200 mL of water to form a slurry. Carbon dioxide gas was bubbled through the slurry until the pH of such was about 6.5. The slurry was filtered and washed with a further 500 mL of water. The filter cake was then re-slurried in sufficient water to produce a slurry containing 50% solids. Glacial acetic acid (5g) was added to the final
- 25 slurry, which was then heated to 85°C.

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A quantity of a pseudo-boehmite suspension was added to the slurry. The pseudo-boehmite suspension was prepared by the dispersion 50 g of a commercial pseudo-boehmite (either Catapal B (supplied by Vista Condea) or HiQ X (supplied by Alcoa World Chemicals)) in 200 g of 85°C water. After the mix  
5 returned to 85°C 5 g of glacial acetic acid was added.

After mixing for several minutes the slurry to which the pseudo-boehmite suspension was added was then spray dried. Throughout the spray drying the off gas temperature was maintained at 180°C. Portions of the product were calcined at 500°C in a muffle furnace for one hour.

#### 10 Example 3

One kilogram of alumina particles with a  $D_{50}$  of 15.3  $\mu\text{m}$  was added to 1200 mL of water to form a slurry. Carbon dioxide gas was bubbled through the slurry until the pH of such was about 6.5. The slurry was filtered and washed with a further 500 mL of water. The filter cake was then re-slurried in sufficient water to produce  
15 a slurry containing 50% solids. Glacial acetic acid (5g) was added to the final slurry, which was then heated to 85°C.

A quantity of a pseudo-boehmite suspension was added to the slurry. The pseudo-boehmite suspension was prepared by the dispersion 20 gm of a commercial pseudo-boehmite (either Catapal B (supplied by Vista Condea) or HiQ  
20 X (supplied by Alcoa World Chemicals)) in 200 g of 85°C water. After the mix returned to 85°C 5 g of glacial acetic acid was added.

After mixing for several minutes the slurry to which the pseudo-boehmite suspension was added was then spray dried. Throughout the spray drying the off gas temperature was maintained at 180°C. Portions of the product were calcined  
25 at 500°C in a muffle furnace for one hour.



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Example 4

Alumina particles with a  $D_{50}$  of 15.3  $\mu\text{m}$  were slurried in of water. Carbon dioxide gas was bubbled through the slurry until the pH of such was about 6.5. The slurry was filtered and washed with a further 500 mL of water, then dried. The powder  
5 was then dry ground in a Jet Mill. One kilogram of the ground alumina particles was added to 800 mL of water to form a slurry.. Glacial acetic acid (5g) was added to the final slurry, which was then heated to 85°C.

A quantity of a pseudo-boehmite suspension was added to the slurry. The pseudo-boehmite suspension was prepared by the dispersion 10 gm of a  
10 commercial pseudo-boehmite (either Catapal B (supplied by Vista Condea) or HiQ X (supplied by Alcoa World Chemicals)) in 200 g of 85°C water. After the mix returned to 85°C 5 g of glacial acetic acid was added.

After mixing for several minutes the slurry to which the pseudo-boehmite suspension was added was then spray dried. Throughout the spray drying the off  
15 gas temperature was maintained at 180°C. Portions of the product were calcined at 500°C in a muffle furnace for one hour.

Example 5

Alumina particles with a  $D_{50}$  of 15.3  $\mu\text{m}$  were slurried in water. Carbon dioxide gas was bubbled through the slurry until the pH of such was about 6.5. The slurry was  
20 filtered and washed with a further 500 mL of water, then dried. The powder was then dry ground in a Jet Mill. One kilogram of the ground alumina particles was added to 820 mL of water to form a slurry. Glacial acetic acid (4.4g) was added to the final slurry, which was then heated to 85°C.

A quantity of a pseudo-boehmite suspension was added to the slurry. The pseudo-boehmite suspension was prepared by the dispersion 10 gm of a  
25 commercial pseudo-boehmite (either Catapal B (supplied by Vista Condea) or HiQ X (supplied by Alcoa World Chemicals)) in 200 g of 85°C water. After the mix returned to 85°C, 0.7 g of glacial acetic acid was added.

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After mixing for several minutes the slurry to which the pseudo-boehmite suspension was added was then spray dried. Throughout the spray drying the off gas temperature was maintained at 180°C. Portions of the product were calcined at 500°C in a muffle furnace for one hour.

#### 5 Example 6

Alumina particles with a  $D_{50}$  of 15.3  $\mu\text{m}$  were slurried in water. Carbon dioxide gas was bubbled through the slurry until the pH of such was about 6.5. The slurry was filtered and washed with a further 500 mL of water, then dried. The powder was then dry ground in a Jet Mill. One kilogram of the ground alumina particles was  
10 added to 800 mL of water to form a slurry. Glacial acetic acid (5g) was added to the final slurry, which was then heated to 85°C.

A quantity of a pseudo-boehmite suspension was added to the slurry. The pseudo-boehmite suspension was prepared by the dispersion 20 gm of a commercial pseudo-boehmite (either Catapal B (supplied by Vista Condea) or HiQ  
15 X (supplied by Alcoa World Chemicals)) in 200 g of 85°C water. After the mix returned to 85°C 5 g of glacial acetic acid was added.

After mixing for several minutes the slurry to which the pseudo-boehmite suspension was added was then spray dried. Throughout the spray drying the off gas temperature was maintained at 180°C. Portions of the product were calcined  
20 at 500°C in a muffle furnace for one hour.

#### Example 7

One kilogram of alumina particles with a  $D_{50}$  of 15.3  $\mu\text{m}$  was added to 800 mL of water to form a slurry. Carbon dioxide gas was bubbled through the slurry until the pH of such was about 6.5. Glacial acetic acid (5g) was added to the slurry,  
25 which was then heated to 85°C. This slurry was ground for 30 minutes in a laboratory jar mill.

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A quantity of a pseudo-boehmite suspension was added to the slurry. The pseudo-boehmite suspension was prepared by the dispersion 20 gm of a commercial pseudo-boehmite (either Catapal B (supplied by Vista Condea) or HiQ X (supplied by Alcoa World Chemicals)) in 200 g of 85°C water. After the mix  
5 returned to 85°C 5 g of glacial acetic acid was added.

After mixing for several minutes the slurry to which the pseudo-boehmite suspension was added were then spray dried. Throughout the spray drying the off gas temperature was maintained at 180°C. Portions of the product were calcined at 500°C in a muffle furnace for one hour.

#### 10 Example 8

One kilogram of alumina particles with a  $D_{50}$  of 15.3  $\mu\text{m}$  was added to 1200 mL of water to form a slurry. Carbon dioxide gas was bubbled through the slurry until the pH of such was about 6.5. The slurry was filtered and deliquored. The filter cake was then reslurried in sufficient water to produce a slurry containing 50%  
15 solids. Glacial acetic acid (5g) was added to the final slurry, which was then heated to 85°C. This slurry was ground for 30 minutes in a laboratory jar mill.

A quantity of a pseudo-boehmite suspension was added to the slurry. The pseudo-boehmite suspension was prepared by the dispersion 20 gm of a commercial pseudo-boehmite (either Catapal B (supplied by Vista Condea) or HiQ  
20 X (supplied by Alcoa World Chemicals)) in 200 g of 85°C water. After the mix returned to 85°C 5 g of glacial acetic acid was added.

After mixing for several minutes the slurry to which the pseudo-boehmite suspension was added was then spray dried. Throughout the spray drying the off gas temperature was maintained at 180°C. Portions of the product were calcined  
25 at 500°C in a muffle furnace for one hour.

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Example 9

One kilogram of alumina particles with a  $D_{50}$  of 15.3  $\mu\text{m}$  was added to 1200 mL of water to form a slurry. Carbon dioxide gas was bubbled through the slurry until the pH of such was about 6.5. The slurry was filtered and washed with a further  
5 500 mL of water. The filter cake was then reslurried in sufficient water to produce a slurry containing 50% solids. Glacial acetic acid (5g) was added to the slurry, which was then heated to 85°C. This slurry was ground for 30 minutes in a laboratory jar mill.

A quantity of a pseudo-boehmite suspension was added to the slurry. The  
10 pseudo-boehmite suspension was prepared by the dispersion 8 gm of a commercial pseudo-boehmite (either Catapal B (supplied by Vista Condea) or HiQ X (supplied by Alcoa World Chemicals)) in 200 g of 85°C water. After the mix returned to 85°C 5 g of glacial acetic acid was added.

After mixing for several minutes the slurry to which the pseudo-boehmite  
15 suspension was added was then spray dried. Throughout the spray drying the off gas temperature was maintained at 180°C. Portions of the product were calcined at 500°C in a muffle furnace for one hour.

Example 10

Alumina particles with a  $D_{50}$  of 15.3  $\mu\text{m}$  were slurried in water. Carbon dioxide gas  
20 was bubbled through the slurry until the pH of such was about 6.5. The slurry was filtered and washed with a further 500 mL of water, then dried. The powder was then dry ground in a Jet Mill. One kilogram of the ground alumina particles was added to 800 mL of water to form a slurry. Glacial acetic acid (5g) was added to the final slurry.

25 A quantity of a pseudo-boehmite suspension was added to the slurry. The pseudo-boehmite suspension was prepared by the dispersion 40 gm of a commercial pseudo-boehmite (either Catapal B (supplied by Vista Condea) or HiQ

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X (supplied by Alcoa World Chemicals)) in 200 g of water at room temperature. 5 g of glacial acetic acid was added to this mix.

After mixing for several minutes the slurry to which the pseudo-boehmite suspension was added was then spray dried. Throughout the spray drying the off gas temperature was maintained at 180°C. Portions of the product were calcined at 500°C in a muffle furnace for one hour.

#### Example 11

Alumina particles with a  $D_{50}$  of 15.3  $\mu\text{m}$  were slurried in water. Carbon dioxide gas was bubbled through the slurry until the pH of such was about 6.5. The slurry was filtered and washed with a further 500 mL of water, then dried. The powder was then dry ground in a Jet Mill. One kilogram of the ground alumina particles was added to 800 mL of water to form a slurry. Glacial acetic acid (5g) was added to the final slurry.

A quantity of a pseudo-boehmite suspension was added to the slurry. The pseudo-boehmite suspension was prepared by the dispersion 20 gm of a commercial pseudo-boehmite (either Catapal B (supplied by Vista Condea) or HiQ X (supplied by Alcoa World Chemicals)) in 200 g of water. 5 g of glacial acetic acid was added to the mix.

After mixing for several minutes the slurry to which the pseudo-boehmite suspension was added was then spray dried. Throughout the spray drying the off gas temperature was maintained at 180°C. Portions of the product were calcined at 500°C in a muffle furnace for one hour.

A summary of the test conditions for Examples 1 to 11 appears in Table 1, below.

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Table 1

| Example | Dust D <sub>50</sub><br>(µm) | Filtered<br>? | Washed<br>? | How<br>Milled | SD Feed<br>D50, (µm) | Binder<br>% | Peptise T, °C |
|---------|------------------------------|---------------|-------------|---------------|----------------------|-------------|---------------|
| 1       | 15.3                         | No            | No          | No            | 15.3                 | 5%          | 85            |
| 2       | 15.3                         | Yes           | Yes         | No            | 15.3                 | 5%          | 85            |
| 3       | 15.3                         | Yes           | Yes         | No            | 15.3                 | 2%          | 85            |
| 4       | 15.3                         | Yes           | Yes         | Dry           | 4.6                  | 1.0         | 85            |
| 5       | 15.3                         | yes           | yes         | Dry           | 4.6                  | 1.0         | 85            |
| 6       | 15.3                         | Yes           | Yes         | Dry           | 4.6                  | 2.0         | 85            |
| 7       | 15.3                         | No            | No          | Wet           | 5.0                  | 2.0         | 85            |
| 8       | 15.3                         | Yes           | No          | Wet           | 5.3                  | 2.0         | 85            |
| 9       | 15.3                         | Yes           | Yes         | Wet           | 5.4                  | 0.8         | 85            |
| 10      | 15.3                         | Yes           | Yes         | Dry           | 4.6                  | 4.0         | 20            |
| 11      | 15.3                         | Yes           | Yes         | Dry           | 4.6                  | 2.0         | 20            |

Product samples were analysed for soda content so as to distinguish the effect of washing the feed dust, as it was suspected that soda content may adversely affect boehmitic gel formation. The results of the soda content analyses of the agglomerates appear in Table 2, below

Table 2

| Example | 1    | 2, 3 | 4, 5,<br>6, 10, 11 | 7    | 8    | 9,   |
|---------|------|------|--------------------|------|------|------|
| % soda  | 0.78 | 0.33 | 0.27               | 0.77 | 0.30 | 0.33 |

Samples of the micro agglomerates were analysed for particle size distribution. The results of the particle size distribution analysis are given in Table 3, below. For comparative purposes the size analysis of regular smelting grade alumina (SGA) is also included.

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Table 3

| Cumulative percent passing size | 1000 $\mu\text{m}$ | 300 $\mu\text{m}$ | 212 $\mu\text{m}$ | 150 $\mu\text{m}$ | 106 $\mu\text{m}$ | 75 $\mu\text{m}$ | 53 $\mu\text{m}$ |
|---------------------------------|--------------------|-------------------|-------------------|-------------------|-------------------|------------------|------------------|
| Example 1                       | 100                | 79.8              | 54.4              | 35.5              | 21.4              | 16.3             | 13.7             |
| Example 2                       | 100                | 84.2              | 61.2              | 36.7              | 15.5              | 5.7              | 2.1              |
| Example 3                       | 100                | 82.7              | 58.3              | 34.0              | 13.6              | 4.6              | 1.4              |
| Example 4                       | 100                | 85.5              | 58.3              | 32.3              | 12.9              | 3.9              | 1.0              |
| Example 5                       | 100                | 87.4              | 69.5              | 47.7              | 24.0              | 9.0              | 2.6              |
| Example 6                       | 100                | 83.0              | 51.8              | 27.8              | 10.9              | 3.9              | 1.4              |
| Example 7                       | 100                | 63.1              | 33.8              | 16.7              | 6.8               | 4.2              | 3.5              |
| Example 8                       | 100                | 77.7              | 49.2              | 27.7              | 10.6              | 2.4              | 0.3              |
| Example 9                       | 100                | 91.2              | 72.2              | 48.1              | 24.6              | 9.5              | 2.8              |
| Example 10                      | 100                | 89.9              | 62.4              | 37.6              | 16.6              | 5.7              | 1.7              |
| Example 11                      | 100                | 92.3              | 67.7              | 38.0              | 16.1              | 5.9              | 1.9              |
| SGA1                            | 100                | 99.9              | 99.7              | 95.3              | 70.1              | 34.8             | 13.8             |
| SGA2                            | 100                | 100               | 100               | 94.4              | 42.7              | 15.0             | 4.8              |

In all cases the micro agglomerates formed are of a size slightly coarser than smelting grade alumina, but which is acceptable for the end use.

- 5 The micro agglomerates were also tested for strength using an attrition test wherein 25 g of micro agglomerate was placed on the top screen in a stack on a RoTap, and the RoTap was activated for 5 minutes. A separate sample was placed on the RoTap for 20 minutes. The difference in particle size distribution was used as a comparative breakage test for the samples. The results were
- 10 compared to a sample of smelting grade alumina. The results of this testing are given in Tables 4 and 5. Table 4, below, shows the results of the attrition testing conducted on the discharge from the spray dryer.

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Table 4

| Screen size  | 300 $\mu$ m | 212 $\mu$ m | 150 $\mu$ m | 106 $\mu$ m | 75 $\mu$ m | 53 $\mu$ m | - 53 $\mu$ m |
|--|-------------|-------------|-------------|-------------|------------|------------|--------------|
| (Change in percent of material retained on screen between 5 and 20 minute shaking) |             |             |             |             |            |            |              |
| Example 1  | -19.7       | -25.2       | -17.8       | -0.6        | 1.2        | 0.6        | 61.4         |
| Example 2  | -2.9        | -0.7        | 1.1         | 0.9         | 0.3        | 0.1        | 1.2          |
| Example 3  | -16.9       | -16.4       | 9.2         | 4.6         | 1.9        | 1.0        | 16.6         |
| Example 4  | -1.7        | -1.2        | 0.8         | 1.2         | 0.4        | 0.2        | 0.4          |
| Example 5  | -2.2        | -1.1        | 0.5         | 0.7         | 0.1        | 0.2        | 0.9          |
| Example 6  | -2.3        | 0.3         | 0.8         | 0.4         | 0.1        | 0.3        | 0.5          |
| Example 7  | -36.0       | -28.7       | -14.0       | 11.4        | -0.1       | 1.3        | 66.1         |
| Example 8  | -7.5        | 1.4         | 2.2         | 1.1         | 0.6        | 0.4        | 1.7          |
| Example 9  | -1.4        | -0.9        | 0.5         | 0.6         | 0.2        | -0.1       | 1.2          |
| Example 10   | -0.6        | -0.4        | 0.2         | 0.1         | 0.1        | 0.2        | 0.4          |
| Example 11   | -5.3        | 0.9         | 1.6         | 0.8         | 0.2        | 0.1        | 1.7          |
| SGA1   | -0.1        | -0.1        | -0.5        | -0.5        | -0.4       | 0          | 1.7          |
| SGA 2  | 0           | 0           | -0.5        | -1.1        | 1.0        | 0          | 0.7          |

Of particular interest is the increase in the finest portion of the measured particle size distribution (53  $\mu$ m) and we can see that the micro agglomerates produced in  
 5 examples 2, 4, 5, 6, 8 and 9 are of comparable attrition resistance to smelting grade alumina. Examples 10 and 11 demonstrated acceptable attrition resistance

On the basis of these results it was determined that the product of examples 1, 3 and 7 had unsatisfactory attrition resistance and no further testing was conducted. From the attrition test results of the paired Examples 1 and 2 and also 7 and 8 we  
 10 learn that the soluble soda levels of the alumina dust must be reduced before this pseudo-boehmite binding system can be effectively applied. Apparently the presence of soluble salts interferes with the peptisation of the pseudo-boehmite.

A comparison of examples 2 and 3 with examples 6 and 8 show that to produce attrition resistant product a higher binder level (5% for example 2, 2% in examples  
 15 3 and 6) is required with coarser dusts.

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Table 5, below, shows the results of the attrition testing for micro agglomerates which have been calcined to 500°C.

Table 5

| Screen size  | 300 $\mu$ m | 212 $\mu$ m | 150 $\mu$ m | 106 $\mu$ m | 75 $\mu$ m | 53 $\mu$ m | - 53 $\mu$ m |
|--|-------------|-------------|-------------|-------------|------------|------------|--------------|
| (Change in percent of material retained on screen between 5 and 20 minute shaking) |             |             |             |             |            |            |              |
| Example 2  | -6.6        | 1.0         | 2.1         | 1.2         | 0.6        | 0.3        | 1.4          |
| Example 4  | -1.8        | -1.3        | 0.9         | 1.2         | 0.4        | 0.2        | 0.4          |
| Example 5  | -9.4        | -4.1        | 3.3         | 4.1         | 1.0        | 1.0        | 4.0          |
| Example 6  | -10.9       | 3.1         | 3.6         | 1.4         | 0.8        | 0.3        | 1.7          |
| Example 8  | -15.8       | 4.8         | 4.6         | 2.1         | 0.9        | 0.8        | 2.7          |
| Example 9  | -5.8        | -1.6        | 2.5         | 2.0         | 1.0        | 0.4        | 1.5          |
| Example 10   | -2.0        | -0.6        | 0.8         | 0.9         | 0.3        | 0.1        | 0.5          |
| Example 11   | -5.9        | -19.4       | -9.8        | 11.5        | 3.3        | 2.5        | 17.8         |
| SGA1   | -0.1        | -0.1        | -0.5        | -0.5        | -0.4       | 0          | 1.7          |
| SGA 2  | 0           | 0           | -0.5        | -1.1        | 1.0        | 0          | 0.7          |

- 5 Calcination to 500°C causes any gibbsite, which may be present in the dust, and the pseudo-boehmite added to dehydroxylate. Attrition resistance remains generally acceptable Whilst demonstrating acceptable attrition resistance down to the 2% binder level before calcination, Examples 10 and 11 showed unsatisfactory attrition resistance below 4% binder concentration after calcination.
- 10 From the preceding results, it can be seen that the method of the present invention is highly effective at agglomerating alumina particles into micro-agglomerates of appropriate size and resistance to attrition to be incorporated into smelting grade alumina. This is achieved using levels of binder much lower than that utilised in the prior art, affording cost savings and industrial hygiene benefits.
- 15 It is envisaged that a catalyst metal may be added to the slurry to produce a high surface area catalyst product on an alumina binder.

Modifications and variations such as would be apparent to the skilled addressee are considered to fall within the scope of the present invention.

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**The Claims Defining the Invention are as Follows**

1. A method for the agglomeration of alumina particles, the method characterised by the steps of:
  - adding a quantity of pseudo-boehmite to the alumina particles; and
  - 5        spray drying the mixture so formed to produce agglomerated granules.
2. A method according to claim 1 characterised in that the pseudo-boehmite is added as an aqueous suspension.
3. A method according to claim 2 characterised in that the aqueous suspension of pseudo-boehmite is formed at a temperature between about 15 and 100°C.
- 10    4. A method according to claim 2 or 3 characterised in that the aqueous suspension of pseudo-boehmite is formed at a temperature above about 80°C.
5. A method according to claim 4 characterised in that the aqueous suspension of pseudo-boehmite is formed at a temperature above about 85°C.
- 15    6. A method according to any one of claims 2 to 5 characterised in that a quantity of acid is added to the aqueous suspension of pseudo-boehmite such that the pH of such is between about 2 and 6.
7. A method according to claim 6 characterised in that a quantity of acid is added to the aqueous suspension of pseudo-boehmite such that the pH of such is approximately 3.
- 20    8. A method according to claim 6 or 7 characterised in that the acid is monoprotic.
9. A method according to claim 8 characterised in that the acid is acetic acid.

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10. A method according to any one of the preceding claims characterised in that, before the step of adding a quantity of pseudo-boehmite to the alumina particles, the present invention comprises the step of grinding the alumina particles to a  $D_{50}$  of less than 12  $\mu\text{m}$ .
- 5 11. A method according to claim 10 characterised in that the alumina particles are ground to a  $D_{50}$  of less than about 9  $\mu\text{m}$ .
12. A method according to claim 11 characterised in that the alumina particles are ground to a  $D_{50}$  of about 5  $\mu\text{m}$ .
- 10 13. A method according to any one of the preceding claims characterised in that a quantity of water is added to the alumina particles to form a slurry, the slurry then being subjected to grinding.
14. A method according to any one of claims 1 to 12 characterised in that the alumina particles are subjected to dry grinding before a quantity of water is added to form a slurry.
- 15 15. A method according to claim 14 characterised in that the quantity of water may be provided by way of the aqueous suspension of pseudo-boehmite.
16. A method according to any one of claims 13 to 15 characterised in that the slurry is of a high density.
- 20 17. A method according to claim 16 characterised in that the slurry comprises at least 50% solids.
18. A method according to claim 16 characterised in that the slurry comprises between about 40 and 60% solids.
19. A method according to any one of claims 13 to 18 characterised in that a viscosity modifier is added to the slurry.

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20. A method according to claim 19 characterised in that the viscosity modifier contains one or more of acetic acid, citric acid or a polyacrylate.
21. A method according to claim 19 characterised in that the viscosity modifier is added such that the viscosity of the slurry is less than about 4 cp.
- 5 22. A method according to any one of claims 19 to 21 characterised in that the viscosity modifier is acetic acid.
23. A method according to claim 22 characterised in that sufficient acetic acid is introduced such that the concentration of the acetic acid in the slurry is between about 0.2 and 1.5% by weight of the alumina particles.
- 10 24. A method according to any one of the preceding claims characterised in that before the quantity of pseudo-boehmite is added to the alumina particles, the method comprises the additional steps of:
- neutralising, dewatering and washing the alumina particles.
- 15 25. A method according to claim 24 characterised in that dewatering is achieved by way of filtration.
26. A method according to claim 24 characterised in that dewatering is achieved by way of centrifugation.
27. A method according to any one of claims 24 to 26 characterised in that carbon dioxide is used to neutralise the alumina particles.
- 20 28. A method according to any one of claims 24 to 27 characterised in that the step of neutralising, dewatering and washing the alumina particles is carried out before grinding the alumina particles.
29. A method according to any one of the preceding claims characterised by the step of:

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heating the agglomerated granules.

30. A method according to claim 29 characterised in that the agglomerated particles are dehydroxylated by heating to approximately 300°C.

31. A method according to claim 29 characterised in that the agglomerated  
5 granules are calcined above 500°C.

32. Agglomerated alumina particles produced by any one of the method of any one of claims 1 to 31.

33. A method for the agglomeration of alumina particles substantially as described herein with reference to any one of Examples 1 to 11.

10 34. Agglomerated alumina particles substantially as described herein with reference to any one of Examples 1 to 11.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/AU01/00213

|   |  |   |
|---|--|---|
| <b>A. CLASSIFICATION OF SUBJECT MATTER</b>  |  |   |
| Int. Cl. <sup>7</sup> : C22B 1/243  |  |   |
| According to International Patent Classification (IPC) or to both national classification and IPC   |  |   |
| <b>B. FIELDS SEARCHED</b>   |  |   |
| Minimum documentation searched (classification system followed by classification symbols)<br>C22B 1/243, C01F 7/02, B01J 2/28, 2/02   |  |   |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched<br>AU:IPC as above  |  |   |
| Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)<br>WPAT: ALUMIN+ or AL2O3  |  |   |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>   |  |   |
| Category*   | Citation of document, with indication, where appropriate, of the relevant passages       | Relevant to claim No.   |
| A   | WO 94/14988 A (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION) 7 July 1994 |   |
| A   | US 4579839 A (Pearson) 1 April 1986  |   |
| A   | US 5296177 A (Thé et al.) 22 March 1994  |   |
| <input type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex  |  |   |
| <p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> |  |   |
| Date of the actual completion of the international search<br>8 May 2001   |  | Date of mailing of the international search report<br>10 May 2001     |
| Name and mailing address of the ISA/AU<br>AUSTRALIAN PATENT OFFICE<br>PO BOX 200, WODEN ACT 2606, AUSTRALIA<br>E-mail address: pct@ipaustralia.gov.au<br>Facsimile No. (02) 6285 3929   |  | Authorized officer<br><br>JOHN DEUTS<br>Telephone No : (02) 6283 2146 |

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
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This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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| END OF ANNEX                           |         |    |          |                      |          |    |          |